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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C09K 5/04, C10M 169/04	A1	(11) International Publication Number: WO 94/26835 (43) International Publication Date: 24 November 1994 (24.11.94)
(21) International Application Number: PCT/NL94/00112 (22) International Filing Date: 16 May 1994 (16.05.94) (30) Priority Data: 9300834 14 May 1993 (14.05.93) NL (71)(72) Applicant and Inventor: ENGELS, Bernardina, Carolina, Maria [NL/NL]; Kloosterstraat 14, NL-5921 HC Venlo-Blerick (NL). (74) Agent: TIMMERMANS, Anthonius, Cornelis, Theodorus; Octrooibureau Zuid, Bureau voor Merken en Modellen B.V., P.O. Box 2287, NL-5600 CG Eindhoven (NL).		(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DE (Utility model), DK, DK (Utility model), ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>In English translation (filed in Dutch).</i>
(54) Title: COOLING DEVICE (57) Abstract <p>A cooling device is equipped with a system equipped with a compressor, a damper and connecting pipes and this system is filled with a cooling medium, which cooling medium is composed of a mixture of a cooling agent for purposes of cooling, a mineral lubricating oil, and one or more hydrocarbons.</p>		

Title: Cooling Device

Description

5 The invention pertains to a cooling device equipped with a system containing a compressor, a damper and connecting pipes and filled with a cooling medium.

Cooling devices of the type described above are known in many embodiments and for use in various applications. Such applications
10 are partially industrial and partly domestic in nature.

The system which, as indicated above contains a compressor, a damper and connecting pipes is, as is generally known, filled with a cooling medium for which purposes a wide variety of agents are used. Many of these media are in principle detrimental to the
15 environment, especially when they contain chlorine-related compounds. In many cases, the chlorine-based medium employed is made from CFC-12 or HCFC-22, often known under the names R-12 and R-22. R-12 is chemically composed as dichloro-difluoro-methane, while R-22 is mono-chloro-difluoro-methane. As is evident from the
20 chemical formulas for them, both agents contain a considerable amount of chlorine which can be released into the environment in the case, for example, of leakage or the scrapping of the cooling device in question. In particular, it would appear that the ozone layer is affected by the release of this chlorine, a situation
25 with severe implications for the environment. It is therefore desirable to avoid the usage of these cooling media; they either are already or will shortly be banned in various countries. For this reason, suggestions have been made concerning the replacement of these disadvantageous cooling agents by other especially
30 chlorine-free alternatives. One of the most promising agents is 1,1,1 tetra-fluoro-ethane, which is also known as HFC-134a or R-134a. The properties of this cooling agent are comparable to the properties of the much-used R-12 and it is therefore extremely useful as a worthy replacement for R-12.

35 In a cooling device equipped with a system containing a compressor, a damper and connecting pipes, it is necessary that a lubricating means be present in addition to the actual cooling agents, which cooling agents can be, for example, of the types indicated in the aforementioned. This lubricating means must

obviously be compatible with the cooling agents in use; that is to say that the correct functioning thereof must not be disturbed. In the case of the known cooling agents R-12 and R-22, use is generally made of a mineral lubricating oil. When a chlorine-free cooling agent is used, such as for example R-134a, the use of a mineral lubricating oil is not possible because such an oil is not miscible with the cooling agent itself. Mixing with the cooling agent is, however, necessary in the cold portion of the circuit in order to ensure a mix with a sufficiently low viscosity and one which stays fluid and does not remain behind in the damper to lead to blockages. Furthermore, the correct viscosity is also desired during the firing of the compressor in order to ensure a beneficial running in of same.

If a chlorine-free cooling agent is used (for example R-134a which is currently marketed by the chemicals' industry for this very purpose), the use of a mineral lubricating oil such as has been used up until now is no longer possible as a result of the polar-molecule character of R-134a in contrast with R-12. For this reason, when R-134a is used it is normal to make use on an ester - specifically a polyester - as lubrication means. These lubricating means are, however, much more sensitive and more hygroscopic compared to mineral oils and their use can lead to chemical reactions taking place in the cooling circuit, whereby the correct functioning of this circuit is inhibited by (usually) blockage. Because of this, the manufacturing of equipment for the use of R-134a is more difficult because much stricter demands have to be made in respect of dampness, the process followed, the specification of components, etc. This obviously leads to a higher cost-price, although the set goal of environmental friendliness is actually achieved. It would therefore be desirable if, in the case of chlorine-free cooling agents such as R-134a, mineral oil could be used. This is, however, seeing as how a mineral oil is immiscible with such chlorine-free cooling agents, impossible.

A particular difficulty arises when one desires to convert an existing cooling device, where R-12 has been used in conjunction with a mineral oil, to a device with a chlorine-free cooling agent such as R-134a. It would appear that it is extremely difficult, in fact to all intents and purposes impossible, to clear the entire cooling circuit of the mineral lubricating means to a degree such

that the aforementioned problems in the case of the replacement by a chlorine-free cooling agent do not occur. With totally new installations, this problem obviously does not arise.

It is therefore the aim of the invention to obviate the problem of the use of a chlorine-free cooling agent such as R-134a in new equipment and in the case of the modification of existing equipment which operates with a chlorine-based cooling agent and a mineral oil, without having to resort to the use of rigorous cleaning procedures or a less desirable ester such as a polyester.

A cooling device in accordance with the invention, equipped with a system containing a compressor, a damper and connecting pipes and filled with a cooling medium, is characterised in that the cooling means are composed of a mixture of a chlorine-free cooling agent, a mineral lubricating oil, and one or more of the hydrocarbons propane, iso-butane, cyclo-propane or dimethyl-ether.

It has transpired that the addition of one or more of the aforementioned substances to the chlorine-free cooling agent makes it possible to use a mineral lubricating oil without this leading to a reduction of the cooling properties of the mixture (in some cases it actually improves them).

In general, it is not necessary and is in fact undesirable to compose the mixture of more than 20 percent by weight of hydrocarbons, due to a possible poor inter-mixing and the flammability of the hydrocarbons. A percentage lower than one percent by weight obviously has little effect and shall therefore only be applied in exceptional circumstances.

If, for cooling-related considerations, a percentage-by-weight of 5 to 15% hydrocarbons must be used and the risk of fire increases accordingly, the percentage of hydrocarbons can be lowered to a level between 5 and 15% by the addition of a second cooling agent, for which purposes penta-fluoro-ethane (HFC-125/R125) has demonstrated particular usefulness. The cooling agent is then preferably composed of a mixture of 80-90% by weight of HFC-134a/R134a and 0.5-5% by weight of HFC-125/R125.

In a method for the manufacture of a cooling device in accordance with the invention, whereby an existing cooling device using a mixture of a chlorine-based cooling agent and a mineral lubricating oil is used as a basis, whereby this mixture is removed and replaced by a mixture of a chlorine-free cooling agent

and one or more of the hydrocarbons propane, iso-butane, cyclo-
propane or dimethyl-ether, it can be desirable that the
replacement mixture introduced also contains a quantity of mineral
lubricating oil as an additive. To this end, the quantity of
5 mineral oil still present in the system is supplemented with new
oil to reach a level necessary to ensure proper functioning. In
most cases, it is possible to assume without undue doubt that the
chlorine-based cooling agent can be replaced by a mixture of a
chlorine-free agent and/or multiple hydrocarbons.

10 It is to be noted that it is of itself known (see the
publication of R. Camporese et al in Proceedings - Volume 1, July
14-17 1992 Purdue University, West Lafayette, Indiana, USA) that
use can be made of a mixture of R-134a and a small amount of
propane in a cooling device. If this mixture is used in a so-
15 called "retrofit" of an installation which contained R-12 and a
lubricating oil, the publication assumes that the lubricating
means are also replaced - a situation which is understandable
because, as has already been explained in the aforementioned, a
polyester is always used when R-134a is applied, while, on the
20 other hand, a mineral oil is always used as a lubricant when R-12
is used.

C L A I M S

1. Cooling device equipped with a system containing a compressor, a damper and connecting pipes and filled with a cooling medium, is characterised in that the cooling means are composed of a mixture of a chlorine-free cooling agent, a mineral lubricating oil, and one or more of the hydrocarbons propane, iso-butane, cyclo-propane or dimethyl-ether.

2. Cooling device in accordance with claim 1, characterised in that the total percentage of hydrocarbons comprises 1-20% by weight of the mixture.

3. Cooling device in accordance with claim 1 or 2, characterised in that the cooling agent is 1,1,1 tetra-fluoro-ethane (HFC-134a/R-134a).

4. Cooling device in accordance with claim 1 or 2, characterised in that the cooling agent is a mixture of 1,1,1 tetra-fluoro-ethane (HFC-134a/R-134a) and penta-fluoro-ethane (HFC-125/R125) and that the percentage of hydrocarbons by weight is 5-15%.

5. Cooling device in accordance with claim 4, characterised in that the cooling agent is a mixture of 80-90 percent by weight of HFC-134a/R-134a and 0.5-5 percent by weight of HFC-125/R125.

6. Method for the fabrication of a cooling device in accordance with claim 1, 2, 3, 4, or 5, characterised in that an existing cooling device is used as a basis, which existing cooling device uses as its cooling materials a mixture of a chlorine-based cooling agent and a mineral lubricating oil, and that this mixture is removed and is replaced by a mixture of a chlorine-free cooling agent and one or more of the hydrocarbons propane, iso-butane, cyclo-propane or dimethyl-ether.

7. Method in accordance with claim 6, characterised in that the applied replacement mixture additionally contains a mineral lubricating oil as a supplement.

INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/NL 94/00112

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C09K5/04 C10M169/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C09K C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,Y	WO,A,93 15163 (ALLIED SIGNAL) 5 August 1993 see abstract; claims 1,5,6 ---	1-7
Y	DATABASE WPI Section Ch, Week 9315, Derwent Publications Ltd., London, GB; Class H07, AN 93-121649 & JP,A,5 059 386 (IDEMITSU KOSAN CO LTD) 9 March 1993 see abstract ---	1-7
Y	EP,A,0 496 937 (HITACHI) 5 August 1992 see abstract; claims 1,10 --- -/--	1-7



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

10 August 1994

Date of mailing of the international search report

30.08.94

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INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/NL 94/00112

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 01762 (DU PONT DE NEMOURS) 6 February 1992 see abstract; claim 1 see example 4 ---	1-7
A	EP,A,0 539 952 (MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD) 5 May 1993 see abstract; claims 1,5,6 ---	1-7
A	EP,A,0 402 009 (DU PONT DE NEMOURS) 12 December 1990 see claims 1,2 see page 3, line 51 - page 5, line 5 -----	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

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